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Functionalised Propargyllithium Reagents

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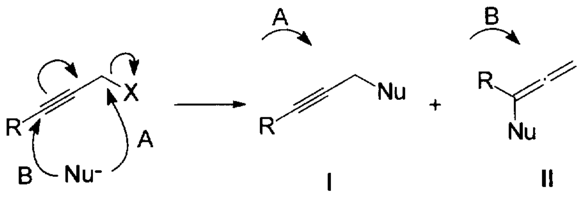
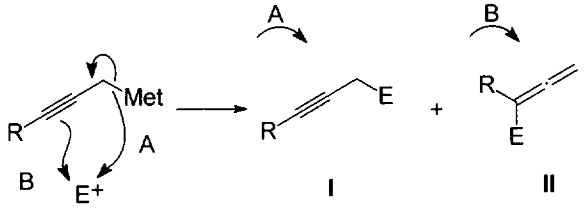
Abstract : The reaction of chlorinated acetylenic ether or amines **1** with lithium and a catalytic amount of DTBB (5%), in the presence of different electrophiles [$\mathrm{Pr^iCHO}$, $\mathrm{Bu^tCHO}$, PhCHO, $\mathrm{Me_2CO}$, $\mathrm{(CH_2)_5CO}$, $\mathrm{Me_3SiCl}$] in THF at -78 or -105°C leads, after hydrolysis with water, to the corresponding products **2**. The same process applied to the previously deprotonated chloroalcohol **4a** or the secondary amine **4b** can be carried out in a two-step reaction giving the expected products **6** by using several electrophiles [$\mathrm{Pr^iCHO}$, $\mathrm{Bu^tCHO}$, PhCHO, $\mathrm{Me_2CO}$, $\mathrm{(CH_2)_5CO}$, $\mathrm{Me_3SiCl}$] at -78°C. © 1997 Elsevier Science Ltd.

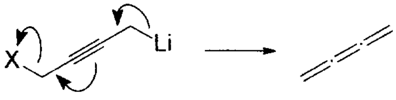
INTRODUCTION

An inherent problem concerning both nucleophilic or electrophilic propargylic substitution is that this process can yield the expected propargylic product of the type **I**, together with the corresponding allenic system of the type **II**, this last one being in many cases the most important.





When at the other propargylic position is a heteroatom, the corresponding organometallic species are, in general, unstable due to their tendency to suffer decomposition, even at low temperatures, to give a δ-elimination reaction which, for instance in the case of the corresponding organolithium compound **III**, would give a cumulenic compound **IV**.[1]

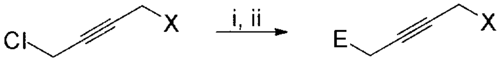


III **IV**

In the last few years we have developed a new methodology consisting in the use of a catalytic amount of an arene for the lithiation of different species (non-halogenated substrates,[2a] functionalised chlorinated precursors,[2b] saturated heterocycles[2c] and polychlorinated compounds[2d]) under very mild reactions conditions. In this paper we describe the preparation of intermediates of the type **III**[3] using this methodology[4] combined or not with working under Barbier-type reactions conditions.[5]

RESULTS AND DISCUSSION

The reaction of functionalised propargyl chlorides **1a-c** with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB; 1:0.1 molar ratio, 5 mol %) in the presence of an equimolecular amount of an electrophile [Pr^iCHO, Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_5CO$, Me_3SiCl] in THF at low temperature (-105°C for compound **1a** and -78°C for compounds **1b** and **1c**; see Table 1) led, after hydrolysis with water, to the corresponding compounds **2** in moderate yields (Scheme 1 and Table 1).



1a: X= OTHP
1b: X= $N[(CH_2)_2]_2O$
1c: X= $N(CH_2CH=CH_2)_2$

2aa-cf

Scheme 1. *Reagents and conditions*: i, Li, DTBB cat. (5 mol %), E^+ = Pr^iCHO, Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_5CO$, Me_3SiCl, THF, -105 or -78°C; ii, H_2O, -105 or -78 to 20°C.

The reaction shown in the Scheme 1 had to be performed under Barbier-type conditions in order to avoid decomposition of the *in situ* formed intermediate of type **III** by δ-elimination: in the presence of the electrophile and at low temperature this decomposition can be avoided in part, so the corresponding intermediate prefers to react mainly with the electrophile.

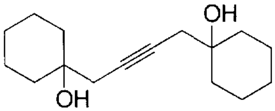
When the process described in the Scheme 1 was applied to the sulphur-containing propargylic chloride **1d**, the only reaction product isolated was the resulting one from a double addition. For instance, using cyclohexanone as electrophile compound **3** was isolated in 60% yield. However, this reaction has not interest from a synthetic point of view, because the same product results from the reaction for 1,4-dichloro-2-butyne under the same reaction conditions.[1]

Table 1. Preparation of Compounds **2**

	Starting	Electrophile	Reaction	Product[a]			
Entry	material	E^+	T (°C)	No.	X	E	Yield (%)[b]	R_f
1	**1a**	$\mathrm{Pr^iCHO}$	-105	**2aa**	OTHP	$\mathrm{Pr^iCHOH}$	50[c]	0.44[d]
2	**1a**	$\mathrm{Bu^tCHO}$	-105	**2ab**	OTHP	$\mathrm{Bu^tCHOH}$	51[c]	0.40[d]
3	**1a**	$\mathrm{Me_2CO}$	-105	**2ad**	OTHP	$\mathrm{Me_2COH}$	45	0.30[d]
4	**1b**	$\mathrm{Pr^iCHO}$	-78	**2ba**	$\mathrm{N[(CH_2)_2]_2O}$	$\mathrm{Pr^iCHOH}$	32	0.38[e]
5	**1b**	$\mathrm{Bu^tCHO}$	-78	**2bb**	$\mathrm{N[(CH_2)_2]_2O}$	$\mathrm{Bu^tCHOH}$	53	0.31[f]
6	**1b**	PhCHO	-78	**2bc**	$\mathrm{N[(CH_2)_2]_2O}$	PhCHOH	53	0.32[g]
7	**1b**	$\mathrm{Me_2CO}$	-78	**2bd**	$\mathrm{N[(CH_2)_2]_2O}$	$\mathrm{Me_2COH}$	54	0.53[g]
8	**1b**	$\mathrm{(CH_2)_5CO}$	-78	**2be**	$\mathrm{N[(CH_2)_2]_2O}$	$\mathrm{(CH_2)_5COH}$	40	0.44[d]
9	**1b**	$\mathrm{Me_3SiCl}$	-78	**2bf**	$\mathrm{N[(CH_2)_2]_2O}$	$\mathrm{Me_3Si}$	53	0.39[f]
10	**1c**	$\mathrm{Pr^iCHO}$	-78	**2ca**	$\mathrm{N(CH_2CH{=}CH_2)_2}$	$\mathrm{Pr^iCHOH}$	49	0.30[f]
11	**1c**	$\mathrm{Bu^tCHO}$	-78	**2cb**	$\mathrm{N(CH_2CH{=}CH_2)_2}$	$\mathrm{Bu^tCHOH}$	36	0.47[f]
12	**1c**	PhCHO	-78	**2cc**	$\mathrm{N(CH_2CH{=}CH_2)_2}$	PhCHOH	75	0.49[f]
13	**1c**	$\mathrm{Me_2CO}$	-78	**2cd**	$\mathrm{N(CH_2CH{=}CH_2)_2}$	$\mathrm{Me_2COH}$	49	0.43[f]
14	**1c**	$\mathrm{(CH_2)_5CO}$	-78	**2ce**	$\mathrm{N(CH_2CH{=}CH_2)_2}$	$\mathrm{(CH_2)_5COH}$	48	0.40[d]
15	**1c**	$\mathrm{Me_3SiCl}$	-78	**2cf**	$\mathrm{N(CH_2CH{=}CH_2)_2}$	$\mathrm{Me_3Si}$	50	0.55[h]

[a] All products **2** were >95% pure (GLC and/or 300 MHz ^{1}H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1**. [c] A *ca.* 1:1 diastereomeric mixture (GLC and/or 300 MHz ^{1}H NMR) was obtained, which could not be separated by TLC. [d] Silica gel, hexane/ethyl acetate: 4/1. [e] Silica gel, ethyl acetate. [f] Silica gel, hexane/ethyl acetate: 7/3. [g] Silica gel, hexane/ethyl acetate: 1/1. [h] Silica gel, hexane/diethyl ether: 7/3.

1d



3

Starting material **1a** was prepared by protection of the corresponding alcohol[6] (obtained from commercially available but-2-yn-1,4-diol with triphenyl phosphine and carbon tetrachloride) under standard conditions[7]. Amines **1b,c** were prepared by treatment of the corresponding dichloride with the appropriate amine in THF.

In the second part of this study we tried to prepare dilithiated intermediates of the type **5**, in which the functionality, bearing a formal negative charge, has less ability to act as a leaving group, so could be possible to avoid decomposition by δ-elimination. Thus, direct treatment of the acetylenic chloroalcohol **4a** with the lithiation mixture described above for compounds **2** at -78°C (method A) gave, a solution of the corresponding dianion **5**, which by reaction with different electrophiles ($\mathrm{Pr^iCHO}$, $\mathrm{Bu^tCHO}$, $\mathrm{Me_2CO}$, $\mathrm{Et_2CO}$) and final hydrolysis with water afforded the expected products **6** (Scheme 2 and Table 2, entries 1-4). Alternatively, the first deprotanation step could be carried out with *n*-butyllithium at -78°C (method B). When this last procedure was applied to the chloroalcohol **4a** followed by lithiation in the presence or not of the electrophile only a dimer of the starting material was detected, even at -90°C and for very short reaction times (5 min) (tandem GLC-MS). The application of this procedure (method B) to the chloroamine **4b** in the reaction with acetone and cyclohexanone as electrophilic reagents under Barbier-type conditions gave compounds **6** with poor yields (Scheme 2 and Table 2, entries 5 and 7). The last reaction gave some better yields when it was performed in a two-step process [Me_2CO, $(CH_2)_5CO$] (method C; Table 2, entries 6 and 8).

4a: Y= O
4b: Y= PhN

5

6aa-be

Scheme 2. *Reagents and conditions* : Method A: i, Li, DTBB cat. (5 mol %); ii, E^+= Pr^{i}CHO, Bu^{t}CHO, Me_2CO, Et_2CO; iii, H_2O, -78 to 20°C. Method B: i, Bu^{n}Li, THF, -78°C; ii, Li, DTBB cat. (5 mol %), E^+= Me_2CO, $(CH_2)_5CO$, THF, -78°C; iii, H_2O, -78 to 20°C. Method C: i, Bu^{n}Li, THF, -78°C; ii, Li, DTBB cat. (5 mol %), then E^+= Me_2CO, $(CH_2)_5CO$, -78°C; iii, H_2O, -78°C to 20°C.

The preparation of starting materials **4a,b** was performed as it was above described for compounds **1**.

Table 2. Preparation of Compounds **6**

	Starting		Electrophile	Product[a]				
Entry	material	Method[b]	E^+	No.	Y	E	Yield (%)[c]	R_f
1	**4a**	A	Pr^{i}CHO	**6aa**	O	Pr^{i}CHOH	54	0.30[d]
2	**4a**	A	Bu^{t}CHO	**6ab**	O	Bu^{t}CHOH	47	0.28[e]
3	**4a**	A	Me_2CO	**6ad**	O	Me_2COH	33	0.40[e]
4	**4a**	A	Et_2CO	**6ag**	O	Et_2COH	62	0.30[f]
5	**4b**	B	Me_2CO	**6bd**	PhN	Me_2COH	24	0.35[g]
6	**4b**	C	Me_2CO	**6bd**	PhN	Me_2COH	36	0.35[g]
7	**4b**	B	$(CH_2)_5CO$	**6be**	PhN	$(CH_2)_5COH$	15	0.31[h]
8	**4b**	C	$(CH_2)_5CO$	**6be**	PhN	$(CH_2)_5COH$	24	0.31[h]

[a] All products **6** were >94% pure (GLC and/or 300 MHz ^1H NMR). [b] Method A: deprotection performed by the lithium-DTBB mixture in a two-step process; Method B: deprotection performed with Bu^{n}Li and lithiation carried out under Barbier-type conditions; Method C: deprotection performed with Bu^{n}Li in a two-step process. [c] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate or diethyl ether) based on the starting material **4**. [d] Silica gel, hexane/ethyl acetate: 1/1. [e] Silica gel, hexane/ethyl acetate: 4/1. [f] Silica gel, hexane/ethyl acetate: 7/3. [g] Silica gel, hexane/diethyl ether: 1/1. [h] Silica gel, hexane/diethyl ether: 7/3.

As a conclusion, we have described here a simple preparation of functionalised propargyl derivatives by chlorine-lithium exchange starting from the corresponding chlorinated precursors. Under the reaction conditions described only acetylenic products were isolated without any contamination with the corresponding allenic compounds.

EXPERIMENTAL PART

General.- FTIR spectra were determined with a Nicolet Impact 400D instrument. Mass spectra were measured with a Shimadzu QP-5000 Mass spectrometer equipped with a GC-17A Gas Chromatograph. ^{1}H and ^{13}C NMR spectra were recorded in a Bruker AC-300 using $CDCl_3$ as solvent unless otherwise noted and $SiMe_4$ as internal standard; chemical shifts are given in δ (ppm) and the coupling constants (J) are measured in Hz. ^{13}C NMR assignments were made on the basis of DEPT experiments. MS (EI) were recorded with a Hewlett Packard EM/CG HP-5988A spectrometer. The purity of volatile distilled products and the chromatographic analyses (GLC) were determined with Hewlett Packard HP-5890 instrument equipped with a flame ionisation detector and a 12 m HP-1 capillary column (0.2 mm diam, 0.33 μm film thickness), using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=275°C, T_{column}=60°C (3 min) and 60-270°C (15°C/min). Thin layer chromatography (TLC) was carried out on Scheleicher & Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using a mixture of hexane/ethyl acetate or diethyl ether as eluant; R_f values are given under these conditions. High resolution mass spectra were performed by the corresponding service at the University of Zaragoza. Solvents were dried by standard procedures.[8] Lithium powder (Strem), starting materials, as well as DTBB and the corresponding electrophiles used, were commercially available (Aldrich, Acros, Fluka).

Preparation of 4-Chloro-2-butyn-1-ol (**4a**)[6].- A mixture of 2-butyne-1,4-diol (0.86 g, 10 mmol) and triphenylphosphine (2.3 g, 10 mmol) in CCl_4 (15 ml) was stirred for 48 h. Then, the solvent was evaporated (15 Torr) giving a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) giving the pure title compound (58%): R_f 0.44 (hexane/diethyl ether: 1/1); ν (film) 3400 cm^{-1} (OH); δ_H 2.18 (1H, s, OH), 4.19 (2H, m, CH_2Cl), 4.33 (2H, m, CH_2OH); δ_C 30.3 (CH_2Cl), 50.95 (CH_2OH), 80.4, 84.6 ($C\equiv C$); *m/z* 105 (M^++1, 4.2%), 103 (M^+-1, 13), 69 (67), 68 (55), 55 (14), 53 (12), 52 (12), 51 (27), 50 (16), 42 (10), 41 (100), 40 (36).

*Preparation of 4-Chloro-2-butynyl Tetrahydro-2*H*-2-pyranyl Ether* (**1a**)[9].- A mixture of chloroalcohol **4a** (1.2 g, 14 mmol), 3,4-dihydropyran (1.8 ml, 20 mmol) and a catalytic amount of *p*-toluenesulfonic acid (50 mg) in CH_2Cl_2 (15 ml) was stirred 12 h. The resulting mixture was then washed with 2M sodium hydroxide (3x10 ml), the organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the pure title compound (86%): R_f 0.40 (hexane/ethyl acetate: 9/1); ν (film) 1120, 1027 cm^{-1} (C-O); δ_H 1.52-1.86 (6H, m, 3xring CH_2), 3.54, 3.84 (2H, 2m, ring CH_2O), 4.19 (2H, m, CH_2Cl), 4.30 (1H, ddd, J = 3.0, 2.0, 1.0, C*H*HO), 4.33 (1H, ddd, J = 3.0, 2.0, 1.0, CH*H*O), 4.79 (1H, m, OCHO); δ_C 18.9, 25.2, 30.1 (3xring CH_2), 30.3 (CH_2Cl), 54.1 (CH_2O), 61.9 (ring CH_2O), 80.5, 82.5 ($C\equiv C$), 96.8 (CH); *m/z* 189 (M^++2, 1.6%), 187 (M^+, 4.7), 101 (80), 97 (21), 95 (11), 90 (16), 89 (20), 88 (51), 87 (55), 86 (26), 85 (100), 84 (15), 83 (19), 79 (11), 69 (21), 68 (10), 67 (55), 57 (55), 56 (76), 55 (74), 54 (13), 53 (17), 52 (65), 51 (76), 50 (34), 44 (16), 43 (73), 42 (34), 41 (85), 40 (25).

Preparation of Chloroamines **1b**, **1c** *and* **4b**. *General Procedure*.- A mixture of 1,4-dichloro-2-butyne (10 mmol) and the corresponding amine (see Table 3 for reactions conditions) were stirred in the appropriate solvent (5 ml). Then the mixture was washed with 0.5M hydrochloric acid (3x5 ml), the aqueous layer was basified with 1M sodium hydroxide, extracted with ethyl acetate (3x10 ml), the organic layer dried over anhydrous Na_2SO_4 and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford the title compounds. Yields, physical, spectroscopic and analytical data, as well as the corresponding literature references for known compounds, follow.

4-Morpholino-2-butynyl Chloride (**1b**):[10] (53%) R_f 0.39 (hexane); ν (film) 1955 (C≡C), 1116 cm^{-1} (C-O); δ_H 2.56 (4H, m, $2xNCH_2CH_2O$), 3.34 (2H, m, CH_2N), 3.74 (4H, m, $2xNCH_2CH_2O$), 4.19 (2H, m, $ClCH_2$); δ_C 30.3 ($ClCH_2$), 47.2 (CH_2N), 52.1 (2C, $2xNCH_2CH_2O$), 66.5 (2C, $2xNCH_2CH_2O$), 79.9, 81.4 (C≡C); *m/z* 175 (M^++2, 20%), 173 (M^+, 60), 172 (22), 139 (14), 138 (100), 137 (10), 136 (12), 110 (17), 109 (18), 108 (98), 106 (11), 100 (13), 94 (18), 93 (26), 92 (10), 91 (15), 89 (17), 88 (12), 87 (56), 86 (73), 81 (28), 80 (40), 79 (41), 77 (17), 67 (25), 66 (16), 65 (22), 58 (15), 57 (15), 56 (52), 55 (37), 54 (33), 53 (56), 52 (53), 51 (63), 50 (25), 45 (13), 44 (12), 43 (23), 42 (66), 41 (58), 40 (11).

N,N-*Diallyl-4-chloro-2-butyn-1-amine* (**1c**): (63%) R_f 0.53 (hexane/ethyl acetate: 9/1); ν (film) 1653, 1644 cm^{-1} (C=C); δ_H 3.12 (4H, dd, J = 6.4, 1.2, $2xCH_2CH=CH_2$), 3.42 (2H, m, CH_2N), 4.19 (2H, m, CH_2Cl), 5.16, 5.25 (4H, 2m, $2xCH=CH_2$), 5.84 (2H, m, $2xCH=CH_2$); δ_C 30.7 ($ClCH_2$), 41.6 (CH_2N), 56.4 (2C, $2xCH_2CH=CH_2$), 79.3, 79.8 (C≡C), 118.2 (2C, $2xCH=CH_2$), 135.1 (2C, $2xCH=CH_2$); *m/z* 185 (M^++2, 3%), 183 (M^+, 8), 158 (24), 156 (76), 148 (67), 106 (22), 94 (10), 91 (20), 80 (15), 79 (29), 77 (30), 68 (22), 67 (18), 65 (11), 56 (19), 55 (15), 54 (21), 53 (45), 52 (21), 51 (57), 50 (12), 42 (68), 41 (100), 40 (22) (Found: M^+,183.0820. $C_{10}H_{14}NCl$ requires M, 183.0815).

(4-Chloro-2-butynyl)phenylamine (**4b**): (40%) R_f 0.31 (hexane/diethyl ether: 4/1); ν (film) 3403 (NH), 3052, 3022, 1603, 1505 cm^{-1} (C=CH); δ_H 3.98 (2H, m, CH_2N), 4.12 (2H, m, $ClCH_2$), 4.72 (1H, br s, NH), 6.68, 6.79, 7.22 (5H, 3m, 5xArH); δ_C 30.5 ($ClCH_2$), 33.9 (CH_2N), 77.8, 83.75 (C≡C), 113.5, 118.7, 129.2, 146.7 (6C, ArC); *m/z* 182 (M^++3, 2%), 181 (M^++2, 8.8), 180 (M^++1, 6.9), 179 (M^+, 28), 178 (11), 145 (14), 144 (100), 143 (48), 142 (16), 118 (17), 117 (19), 116 (10), 115 (29), 93 (12), 92 (17), 91 (12), 77 (33), 71 (10), 66 (12), 65 (51), 64 (10), 63 (13), 58 (19), 52 (23), 51 (57), 50 (19) (Found: M^+, 179.0499. $C_{10}H_{10}NCl$ requires M, 179.0502).

Table 3. Reaction Conditions for Compounds **1b,c** and **4b**.

Entry	Product	Amine / mmol	Dichlorobutyne mmol	Solvent / ml	Temperature (°C)	Time (h)
1	**1b**	morpholine / 30	20	THF /10	20	24
2	**1c**	diallylamine / 20	10	THF /10	20	10
3	**4b**	aniline / 10	13	aq. $NaHCO_3$ / 15	60	8

DTBB-Catalysed Lithiation of Compounds **1** *and Reaction with Electrophiles. Isolation of Products* **2**. *General Procedure*.- To a suspension of lithium (150 mg, 21 mmol), and DTBB (52 mg, 0.2 mmol), in THF (5 ml), was slowly added (*ca.* 1h) a solution of the corresponding propargylic chloride **1** (2 mmol) and the electrophile (2 mmol) in THF (2 ml) at -105°C (for compounds **1a**) or -78°C (for compounds **1b,c**). Then, the resulting mixture was hydrolysed with water (10 ml) (acidic-basic treatment with 0.5M HCl and 1M NaOH for compounds derived from **1b,c**), extracted with ethyl acetate (3x10 ml), the organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) yielding the pure title compounds. Yields and physical data are included in Table 1. Spectroscopic and analytical data as well as literature references for known compounds, follow.

*2-Methyl-7-tetrahydro-2*H*-2-pyranyloxy-5-heptyn-3-ol* (**2aa**):[10] Diastereomeric mixture 1/1; ν (film) 3441 (OH), 1954 (C≡C), 1022 cm^{-1} (C-O); δ_H 0.92, 0.96 [12H, 2d, J = 7.0, $2x(CH_3)_2$], 1.60, 1.77 (14H, 2m, 6xring CH_2 and 2xCHCHOH), 2.41 (4H, m, $2xCHCHCH_2$), 3.50 (4H, m, $2xCHCHCH_2$ and 2xring CHHO), 3.85

(2H, m, 2xring CH*H*O), 4.26 (4H, m, 2xCH_2O), 4.81 (2H, t, *J* = 3.2, 2xring CH); δ_C 17.6, 19.1 [4C, 2x$(CH_3)_2$], 18.7, 25.1, 25.35 (6C, 6xring CH_2), 30.3 (2C, 2xCHCH*C*H_2), 32.75 (2C, 2x*C*HCHO), 54.65, 54.7 (2xCH_2O), 62.05 (2C, 2xring CH_2O), 74.8 (2C, 2xCH*C*HO), 78.45, 83.15 (4C, 2xC≡C), 96.95 (2C, 2xring CH); *m/z* 183 (M$^+$-43, 0.5%), 101 (38), 86 (13), 85 (100), 84 (13), 83 (13), 81 (10), 73 (62), 71 (17), 57 (40), 56 (56), 55 (69), 54 (17), 53 (36), 52 (61), 51 (11), 45 (13), 44 (11), 43 (74), 42 (12), 41 (69), 40 (11).

*2,2-Dimethyl-7-tetrahydro-2*H*-2-pyranyloxy-5-heptyn-3-ol* (**2ab**):[11] Diastereomeric mixture 1/1; ν (film) 3454 (OH), 1947 (C≡C), 1022 cm^{-1} (C-O); δ_H 0.91 [18H, s, 2x$(CH_3)_3$], 1.71 (12H, m, 6xring CH_2), 2.25, 2.31 (2H, 2dt, *J* = 9.9, 2.1, 2xC*H*HCHOH), 2.45, 2.50 (2H, 2m, 2xCH*H*CHOH), 3.43 (2H, dd, *J* = 9.9, 2.7, 2xC*H*OH), 3.53, 3.85 (4H, 2m, 2xring CH_2O), 4.22, 4.31 (4H, 2dt, *J* = 15.6, 2.1, 2xCH_2O), 4.81 (2H, def s, 2xOCHO); δ_C 19.0, 22.9, 25.3 (6C, 6xring CH_2), 25.6 [6C, 2x$(CH_3)_3$], 30.2 (C≡CCH_2), 34.5 [2C, 2x$(CH_3)_3$*C*], 54.6, 54.7 (2xCH_2O), 61.9 (2C, 2xring CH_2O), 77.7 (2C, 2xHOCH), 78.2, 84.2 (4C, 2xC≡C), 96.9 (2C, 2xring CH); *m/z* 183 (M$^+$-57, 0.9%), 101 (12), 87 (23), 85 (100), 69 (15), 67 (11), 57 (51), 56 (22), 55 (30), 53 (17), 52 (25), 45 (12), 43 (48), 41 (66).

*2-Methyl-6-tetrahydro-2*H*-2-pyranyloxy-4-hexyn-2-ol* (**2ad**):[11] ν (film) 3415 (OH), 1954 cm^{-1} (C≡C); δ_H 1.31 (6H, s, 2xCH_3), 1.69 (6H, m, 3xring CH_2), 2.42 (2H, m, HOCC*H*$_2$), 3.53, 3.86 (2H, 2m, ring CH_2O), 4.23, 4.33 (2H, 2m, CH_2O), 4.83 (1H, m, CH); δ_C 19.0, 25.3, 30.2 (3xring CH_2), 28.6 (2C, 2xCH_3), 34.4 (HOC*C*H_2), 54.6 (CH_2O), 62.0 (ring CH_2O), 69.9 (COH), 77.2, 82.9 (C≡C), 96.8 (ring CH); *m/z* 143 (M$^+$-69, 2%), 101 (15), 86 (12), 85 (100), 67 (25), 59 (81), 57 (28), 56 (22), 55 (30), 53 (12), 52 (60), 51 (11), 43 (76), 42 (11), 41 (64).

2-Methyl-7-morpholino-5-heptyn-3-ol (**2ba**): ν (film) 3421 (OH), 1963 (C≡C), 1116 cm^{-1} (C-O); δ_H 0.92, 0.96 (6H, 2d, *J* = 6.7, 2xCH_3), 1.78 [1H, m, C*H*$(CH_3)_2$], 2.30-2.40 (2H, m, C*H*$_2$CHOH), 2.55 (4H, def t, *J* = 4.7, 2xNC*H*$_2CH_2O$), 3.26 (2H, t, *J* = 2.1, CH_2N), 3.44-3.50 (1H, m, C*H*OH), 3.74 (4H, def t, *J* = 4.7, 2xNCH_2C*H*$_2$O); δ_C 17.45, 18.7 (2xCH_3), 25.0 (*C*H_2CHOH), 32.7 [*C*H$(CH_3)_2$], 47.5 (CH_2N), 52.3 (2C, 2xN*C*H_2CH_2O), 66.7 (2C, 2xNCH_2*C*H_2O), 76.7 (CHOH), 77.75, 82.4 (C≡C); *m/z* 212 (M$^+$+1, 4%), 211 (M$^+$, 25), 210 (13), 168 (11), 139 (38), 138 (43), 126 (13), 124 (14), 112 (16), 109 (26), 108 (83), 100 (51), 94 (17), 93 (12), 87 (47), 86 (100), 82 (25), 81 (29), 80 (24), 79 (16), 73 (34), 67 (14), 58 (12), 57 (38), 56 (59), 55 (70), 54 (25), 53 (55), 52 (33), 51 (16), 45 (23), 44 (39), 43 (79), 42 (88) (Found: M$^+$, 211.1578. $C_{12}H_{21}NO_2$ requires M, 211.1572).

2,2-Dimethyl-7-morpholino-5-heptyn-3-ol (**2bb**): ν (film) 3419 (OH), 1116 cm^{-1} (C-O); δ_H 0.92 (9H, s, 3xCH_3), 2.27, 2.46 (2H, 2m, C*H*$_2$CHOH), 2.56 (4H, def t, *J* = 4.3, 2xNC*H*$_2CH_2O$), 3.27 (2H, m, CH_2N), 3.42 (1H, m, C*H*OH), 3.75 (4H, def t, *J* = 4.3, 2xNCH_2C*H*$_2$O); δ_C (acetone-d^6) 23.4 (CH_2COH), 26.1 (3C, 3xCH_3), 35.5 [*C*$(CH_3)_3$], 48.0 (CH_2N), 52.9 (2C, 2xN*C*H_2CH_2O), 67.3 (2C, 2xNCH_2*C*H_2O), 78.4 (CHOH), 76.7, 84.6 (C≡C); *m/z* 226 (M$^+$+1, 3%), 225 (M$^+$, 22), 224 (12), 194 (12), 168 (22), 140 (16), 139 (21), 138 (54), 126 (41), 124 (14), 112 (36), 110 (11), 109 (16), 108 (79), 107 (11), 100 (74), 96 (11), 95 (15), 94 (17), 93 (14), 88 (16), 87 (85), 86 (100), 82 (35), 81 (24), 80 (19), 79 (14), 71 (12), 70 (12), 69 (32), 67 (14), 58 (16), 57 (81), 56 (66), 55 (41), 54 (25), 53 (53), 52 (27), 51 (14), 45 (33), 44 (28), 43 (74), 42 (84), 41 (84), 40 (10) (Found: M$^+$, 225.1733. $C_{13}H_{23}NO_2$ requires M, 225.1729).

5-Morpholino-1-phenyl-3-pentyn-1-ol (**2bc**): ν (film) 3403 (OH), 1957 (C≡C), 3085, 3061, 3029, 1602, 1493 (C=CH), 1116 cm^{-1} (C-O); δ_H 2.45 (4H, t, *J* = 4.6, 2xNC*H*$_2CH_2O$), 2.67 (2H, dt, *J* = 6.2, 2.1, C*H*$_2$CHOH), 3.19 (2H, m, CH_2N), 3.70 (4H, m, 2xNCH_2C*H*$_2$O), 4.85 (1H, t, *J* = 6.2, C*H*OH), 7.25-7.40 (5H, m, 5xArH); δ_C (acetone-d^6) 30.35 (*C*H_2CHOH), 47.9 (CH_2N), 52.8 (2C, 2xN*C*H_2CH_2O), 67.2 (2C, 2xNCH_2*C*H_2O), 73.1 (CHOH), 77.6, 82.7 (C≡C), 126.95, 127.9, 128.7, 145.3 (6C, ArC); *m/z* 245 (M$^+$, 4%), 107 (11), 105 (11), 87 (12), 86 (13), 79 (16), 77 (22), 57 (12), 56 (14), 55 (12), 51 (18), 44 (100), 43 (17), 42 (19) (Found: M$^+$, 245.1427. $C_{15}H_{19}NO_2$ requires M, 245.1416).

2-Methyl-6-morpholino-4-hexyn-2-ol (**2bd**): ν (film) 3416 (OH), 1116 cm^{-1} (C-O); δ_H 1.31 (6H, s, 2xCH_3), 2.40 (2H, t, *J* = 2.1, C*H*$_2$COH), 2.56 (4H, t, *J* = 4.7, 2xNC*H*$_2CH_2O$), 3.30 (2H, t, *J* = 2.1, CH_2N), 3.75 (4H, t, *J* = 4.7, 2xNCH$_2$C*H*$_2$O); δ_C (acetone-*d*^{6}) 29.1 (2C, 2xCH$_3$), 34.9 (*C*H$_2$COH), 47.9 (CH$_2$N), 52.9 (2C, 2xN*C*H$_2$CH$_2$O), 67.3 (2C, 2xNCH$_2$*C*H$_2$O), 70.1, 77.45, 83.4 (*C*≡*C*CH$_2$*C*OH); *m/z* 198 (M$^+$+1, 3%), 197 (M$^+$, 19), 182 (18), 139 (33), 138 (55), 109 (19), 108 (85), 100 (46), 94 (15), 93 (12), 87 (61), 86 (83), 81 (16), 80 (18), 79 (17), 77 (13), 67 (11), 59 (100), 57 (35), 56 (43), 55 (22), 54 (16), 53 (27), 52 (29), 51 (15), 44 (22), 43 (77), 42 (59) (Found: M$^+$, 197.1407. $C_{11}H_{19}NO_2$ requires M, 197.1416).

1-(4-Morpholino-2-butynyl)cyclohexanol (**2be**): ν (film) 3420 (OH), 1116 cm^{-1} (C-O); δ_H 1.45-1.67 (10H, m, 5xring CH$_2$), 2.38 (2H, m, C*H*$_2$COH), 2.56 (4H, m, 2xNC*H*$_2$CH$_2$O), 3.29 (2H, m, CH$_2$N), 3.74 (4H, m, 2xNCH$_2$C*H*$_2$O); δ_C 22.1, 25.5, 33.1, 36.8 (6C, 5xring CH$_2$ and *C*H$_2$COH), 47.6 (CH$_2$N), 52.3 (2C, 2xN*C*H$_2$CH$_2$O), 66.7 (2C, 2xNCH$_2$*C*H$_2$O), 70.4, 77.7, 81.6 (*C*≡*C*CH$_2$*C*OH); *m/z* 237 (M$^+$, 11%), 139 (53), 138 (48), 112 (13), 109 (20), 108 (61), 100 (46), 99 (47), 94 (22), 88 (12), 87 (100), 86 (79), 82 (17), 81 (69), 80 (17), 79 (24), 77 (10), 69 (13), 67 (18), 65 (11), 58 (10), 57 (55), 56 (51), 55 (72), 54 (19), 53 (37), 52 (30), 51 (16), 44 (19), 43 (59), 42 (84), 41 (82), 40 (15) (Found: M$^+$, 237.1734. $C_{14}H_{23}NO_2$ requires M, 237.1729).

1-Morpholino-4-trimethylsilyl-2-butyne (**2bf**): ν (film) 2225 (C≡C), 1118 cm^{-1} (C-O); δ_H 0.11 (9H, s, 3xCH$_3$), 1.49 (2H, t, *J* = 2.4, SiCH$_2$), 2.55 (4H, m, 2xNC*H*$_2$CH$_2$O), 3.26 (2H, t, *J* = 2.4, CH$_2$N), 3.74 (4H, m, 2xNCH$_2$C*H*$_2$O); δ_C -2.1 (3C, 3xCH$_3$), 6.9 (SiCH$_2$), 47.7 (CH$_2$N), 52.1 (2C, 2xN*C*H$_2$CH$_2$O), 66.7 (2C, 2xNCH$_2$*C*H$_2$O), 74.75, 72.9 (C≡C); *m/z* 213 (M$^+$+2, 0.5%), 212 (M$^+$+1, 2.3), 211 (M$^+$, 14), 138 (14), 108 (20), 100 (41), 86 (31), 73 (100), 59 (16), 56 (25), 45 (34), 44 (12), 43 (23), 42 (28). (Found: M$^+$, 211.1397. $C_{11}H_{21}NOSi$ requires M, 211.1392).

*7-(*N,N*-Diallylamino)-2-methyl-5-heptyn-3-ol* (**2ca**):[11] ν (film) 3403 (OH), 3079, 1643 (C=CH), 1105 cm^{-1} (C-O); δ_H 0.93, 0.98 (6H, 2d, *J* = 6.7, 2xCH$_3$), 1.80 [1H, m, C*H*(CH$_3$)$_2$], 1.91 (1H, br s, OH), 2.33-2.52 (2H, m, C*H*$_2$CHOH), 3.12 (4H, d, *J* = 6.4, 2xNC*H*$_2$CH=CH$_2$), 3.37 (2H, m, CH$_2$N), 3.46 (1H, m, C*H*OH), 5.16, 5.37 (4H, 2m, 2xCH=C*H*$_2$), 5.84 (2H, ddt, *J* = 17.1, 10.2, 6.4, 2xC*H*=CH$_2$); δ_C 17.65, 18.7 (2xCH$_3$), 25.1 (*C*H$_2$CHOH), 32.8 [*C*H(CH$_3$)$_2$], 41.8 (CH$_2$N), 56.4 (2C, 2xN*C*H$_2$CH=CH$_2$), 77.2 (CHOH), 74.95, 81.8 (C≡C), 118.1 (2C, 2xCH=*C*H$_2$), 135.3 (2C, 2x*C*H=CH$_2$); *m/z* 222 (M$^+$+1, 0.6%), 221 (M$^+$, 3), 220 (10), 206 (16), 194 (60), 188 (18), 149 (11), 148 (43), 134 (28), 122 (37), 120 (20), 110 (33), 108 (31), 107 (13), 106 (20), 96 (43), 94 (24), 93 (18), 91 (21), 82 (19), 81 (34), 80 (27), 79 (33), 77 (17), 73 (66), 71 (10), 70 (81), 69 (14), 68 (49), 67 (26), 57 (17), 56 (45), 55 (100), 54 (35), 53 (58), 52 (16), 51 (16), 45 (15), 44 (29), 43 (90), 42 (73).

*7-(*N,N*-Diallylamino)-2,2-dimethyl-5-heptyn-3-ol* (**2cb**):[11] ν (film) 3411 (OH), 3079, 1643 (C=CH), 1240 cm^{-1} (C-O); δ_H 0.93 (9H, s, 3xCH$_3$), 1.26 (1H, s, OH), 2.27 (1H, ddt, *J* = 16.5, 10.1, 2.1, C*H*HCOH), 2.47 (1H, m, CH*H*COH), 3.11-3.16 (5H, m, 2xNC*H*$_2$CH=CH$_2$ and C*H*HN), 3.37 (1H, m, CH*H*N), 3.41 (1H, m, C*H*OH), 5.16, 5.23 (4H, 2m, 2xCH=C*H*$_2$), 5.84 (2H, ddt, *J* = 17.3, 10.1, 6.7, 2xC*H*=CH$_2$); δ_C 22.9 (*C*H$_2$CHOH), 29.7 (3C, 3xCH$_3$), 34.5 [*C*(CH$_3$)$_3$], 41.8 (CH$_2$N), 56.4 (2C, 2xN*C*H$_2$CH=CH$_2$), 77.1, 77.6 (C≡C), 82.75 (CHOH), 118.0 (2C, 2xCH=*C*H$_2$), 135.4 (2C, 2x*C*H=CH$_2$); *m/z* 235 (M$^+$, 0.8%), 208 (16), 148 (14), 122 (17), 110 (15), 108 (13), 96 (19), 87 (16), 70 (31), 69 (19), 68 (18), 57 (23), 56 (14), 55 (13), 54 (10), 53 (16), 45 (15), 43 (29), 42 (26), 41 (100), 40 (12).

*5-(*N,N*-Diallylamino)-1-phenyl-3-pentyn-1-ol* (**2cc**):[11] ν (film) 3373 (OH), 3078, 3030, 1643, 1494, 1453 cm^{-1} (C=CH); δ_H 2.69 (2H, dt, *J* = 6.4, 2.1, C*H*$_2$CHOH), 3.03 (4H, d, *J* = 6.4, 2xNC*H*$_2$CH=CH$_2$), 3.31 (2H, t, *J* = 2.1, CH$_2$N), 4.84 (1H, t, *J* = 6.4, C*H*OH), 5.13, 5.20 (4H, 2m, 2xCH=C*H*$_2$), 5.79 (2H, ddt, *J* = 17.1, 10.4, 6.7, 2xC*H*=CH$_2$), 7.26-7.42 (5H, m, 5xArH); δ_C 29.7 (*C*H$_2$CHOH), 41.75 (CH$_2$N), 56.3 (2C, 2xN*C*H$_2$CH=CH$_2$), 72.5 (CHOH), 77.5, 81.3 (C≡C), 118.1 (2C, 2xCH=*C*H$_2$), 135.2 (2C, 2x*C*H=CH$_2$), 125.85, 127.8, 128.4, 142.8 (6C, ArC); *m/z* 256 (M$^+$+1, 1%), 255 (M$^+$, 10), 254 (45), 228 (32), 148 (77), 141 (11), 133 (15), 115 (10), 110 (15), 108 (13), 107 (68), 106 (23), 105 (22), 96 (23), 94 (15), 91 (19), 82 (11), 80 (18), 79 (100), 77 (66), 70 (54), 68 (29), 67 (14), 56 (21), 55 (13), 54 (19), 53 (22), 52 (16), 51 (25), 44 (11), 43 (11), 42 (42).

*6-(*N,N*-Diallylamino)-2-methyl-4-hexyn-2-ol* (**2cd**): ν (film) 3384 (OH), 3079, 1643 (C=CH), 1150 cm^{-1} (C-O); δ_H 1.32 (6H, s, 2xCH$_3$), 2.41 (2H, t, *J* = 2.1, C*H*$_2$COH), 3.13 (4H, d, *J* = 6.4, 2xNC*H*$_2$CH=CH$_2$), 3.39 (2H, t, *J* = 2.1, CH$_2$N), 5.16, 5.22 (4H, 2m, 2xCH=C*H*$_2$), 5.84 (2H, ddt, *J* = 16.9, 10.2, 6.4, 2xC*H*=CH$_2$); δ_C

28.6 (2C, 2xCH_3), 34.4 (CH_2COH), 41.7 (CH_2N), 56.4 (2C, 2x$NCH_2CH{=}CH_2$), 69.9, 77.6, 81.7 ($C{\equiv}CCH_2COH$), 118.0 (2C, 2x$CH{=}CH_2$), 135.3 (2C, 2x$CH{=}CH_2$); *m/z* 207 (M^+, 1.5%), 180 (39), 149 (17), 148 (100), 134 (15), 110 (36), 108 (12), 106 (15), 96 (28), 94 (13), 93 (12), 91 (14), 82 (14), 81 (11), 80 (14), 79 (21), 77 (18), 70 (68), 68 (35), 67 (15), 59 (97), 56 (26), 55 (16), 54 (18), 53 (21), 52 (12), 51 (12), 44 (12), 43 (67), 42 (45) (Found: M^+, 207.1618. $C_{13}H_{21}NO$ requires M, 207.1623).

1-[4-(N,N-Diallylamino)-2-butynyl]cyclohexanol (**2ce**):[11] ν (film) 3420 (OH), 3078, 1653 (C=CH), 1153 cm^{-1} (C-O); δ_H 1.47-1.80 (10H, m, 5xring CH_2), 2.39 (2H, t, *J* = 2.1, CH_2COH), 3.13 (4H, d, *J* = 6.7, 2x$NCH_2CH{=}CH_2$), 3.39 (2H, t, *J* = 2.1, CH_2N), 5.16, 5.23 (4H, 2m, 2x$CH{=}CH_2$), 5.84 (2H, ddt, *J* = 17.2, 10.3, 6.7, 2x$CH{=}CH_2$); δ_C 22.2, 25.6, 33.2, 36.9 (6C, 5xring CH_2 and CH_2COH), 41.8 (CH_2N), 56.5 (2C, 2x$NCH_2CH{=}CH_2$), 70.5, 78.0, 81.2 ($C{\equiv}CCH_2COH$), 118.0 (2C, 2x$CH{=}CH_2$), 135.4 (2C, 2x$CH{=}CH_2$); *m/z* 246 (M^+-1, 1.4%), 220 (11), 148 (26), 134 (11), 122 (11), 110 (19), 108 (12), 99 (28), 96 (20), 82 (12), 81 (43), 70 (53), 69 (11), 68 (27), 67 (14), 57 (11), 56 (16), 55 (40), 54 (13), 53 (17), 43 (31), 42 (43), 41 (100), 40 (15).

(N,N-Diallyl)-4-trimethylsilyl-2-butyn-1-amine (**2cf**): ν (film) 3079, 1643, 1418 (C=CH), 2223 (C≡C), 851 cm^{-1} (SiC); δ_H 0.12 (9H, s, 3xCH_3), 1.50 (2H, t, *J* = 2.4, $SiCH_2$), 3.12 (4H, d, *J* = 6.7, 2x$NCH_2CH{=}CH_2$), 3.36 (2H, t, *J* = 2.4, CH_2N), 5.12-5.25 (4H, m, 2x$CH{=}CH_2$), 5.76-5.91 (2H, m, 2x$CH{=}CH_2$); δ_C -2.0 (3C, 3xCH_3), 7.0 ($SiCH_2$), 41.9 (CH_2N), 56.3 (2C, 2x$NCH_2CH{=}CH_2$), 72.85, 82.8 (C≡C), 117.8 (2C, 2x$CH{=}CH_2$), 135.7 (2C, 2x$CH{=}CH_2$); *m/z* 221 (M^+, 2.1%), 148 (10), 110 (14), 73 (100), 45 (21), 44 (24), 43 (16), 42 (20) (Found: M^+, 221.1590. $C_{13}H_{23}NSi$ requires M, 221.1600).

DTBB-Catalysed Lithiation of Compounds **4a** *and Reaction with Electrophiles. Isolation of Products* **6aa-ag**. *Method A*.- To a suspension of lithium (150 mg, 21 mmol), DTBB (52 mg, 0.2 mmol) and the corresponding electrophile (2 mmol) in THF (5 ml) was added a solution of the starting material **4a** (0.21 g, 2 mmol) in THF (2 ml) at -78°C. After *ca.* 1 h stirring at the same temperature, the resulting mixture was worked up as it was described above for compounds **2**. Yields and physical data are included in Table 2. Spectroscopic and analytical data follow.

6-Methyl-2-heptyne-1,5-diol (**6aa**):[11] ν (film) 3355 (OH), 2225 (C≡C), 1027 cm^{-1} (C-O); δ_H 0.92, 0.96 (6H, 2d, *J* = 6.7, 2xCH_3), 1.79 (1H, hept, *J* = 6.7, $CHCHO$), 2.25 (1H, br s, OH), 2.37 (1H, ddt, *J* = 16.5, 7.3, 2.0, $CHHCHO$), 2.46 (1H, m, $CHHCHO$), 3.49 (1H, m, CHO), 4.26 (2H, t, *J* = 2.0, CH_2O); δ_C 17.65, 18.65, (2xCH_3), 24.9, 32.75 ($CHCHCH_2$), 51.15 (CH_2O), 74.9 (CHO), 77.2, 80.7 (C≡C); *m/z* 144 (M^++2, 1%), 98 (16), 83 (30), 73 (13), 72 (68), 57 (24), 55 (22), 44 (17), 43 (100), 41 (52), 40 (51).

6,6-Dimethyl-2-heptyne-1,5-diol (**6ab**):[11] ν (film) 3382 (OH), 1954 (C≡C), 1014 cm^{-1} (C-O); δ_H 0.92 (9H, s, 3xCH_3), 2.27 (1H, ddt, *J* = 16.5, 10.1, 2.1, $CHHCHOH$), 2.44 (1H, br s, OH), 2.47 (1H, dc, *J* = 4.9, 2.1, $CHHCH$), 3.44 (1H, dd, *J* = 10.1, 2.1, CH), 4.27 (2H, m, CH_2OH); δ_C 22.7 ($CHCH_2$), 25.6 (3C, 3xCH_3), 34.6 (CCH), 51.2 (CH_2O), 77.7 (CH), 80.5, 84.1 (C≡C); *m/z* 138 (M^+-18, 1.5%), 87 (51), 85 (14), 81 (12), 71 (16), 69 (37), 57 (100), 56 (12), 55 (24), 53 (37), 52 (97), 51 (10), 45 (33), 43 (64), 42 (10), 41 (87), 40 (13).

5-Methyl-2-hexyne-1,5-diol (**6ad**):[11] ν (film) 3345 (OH), 1954 (C≡C), 1014 cm^{-1}(C-O); δ_H 1.32 (6H, s, 2xCH_3), 2.18 (1H, br s, OH), 2.41 (2H, t, *J* = 2.1, $HOCCH_2$), 4.28 (2H, br s, CH_2OH); δ_C 28.7 (2C, 2xCH_3), 34.3 ($HOCCH_2$), 51.2 (CH_2O), 70.0 ($HOCCH_2$), 77.2, 82.7 (C≡C); *m/z* 110 (M^+-18, 0.6%), 59 (100), 52 (66), 43 (85), 41 (26).

5-Ethyl-2-heptyne-1,5-diol (**6ag**):[11] ν (film) 3354 (OH), 2225 (C≡C), 1016 cm^{-1} (C-O); δ_H 0.89 (6H, t, *J* = 7.5, 2xCH_3), 1.58, 1.59 (4H, 2c, *J* = 7.5, 2xCH_2CH_3), 1.87, 2.20 (2H, 2br s, 2xOH), 2.38 (2H, t, *J* = 2.1, $OCCH_2$), 2.27 (2H, t, *J* = 1.8, CH_2O); δ_C 7.9 (2C, 2xCH_3), 29.6 (CH_2CO), 30.55 (2C, 2xCH_2CH_3), 51.15 (CH_2O), 74.05 (CH_2CO), 81.2, 82.4 (C≡C); *m/z* 128 (M^+-28, 1%), 127 (M^+-29 , 10), 87 (46), 69 (10), 57 (100), 45 (48), 43 (18), 41 (16).

DTBB-Catalysed Lithiation of Compounds **4b** *and Reaction with Electrophiles. Isolation of Products* **6bd-be**. *Methods B and C*.- To a solution of compound **4b** (0.36 g, 2 mmol) in THF (3 ml) was added a solution of *n*-butyllithium in hexane (2.2 mmol) at -78°C. After the addition was completed (*ca.* 1 min) the resulting mixture was submitted to the lithiation process in the presence of the electrophile (Method B) or in a two-step process (Method C) as it was above described for compounds **2** and **6**. Yields and physical data are included in Table 2. Spectroscopic and analytical data follow.

2-Methyl-6-phenylamine-4-hexyn-2-ol (**6bd**): ν (film) 3393, 3295 (NH, OH), 2114 (C≡C), 1603, 1506 cm^{-1} (C=CH); δ_H 1.37 (6H, s, 2xCH_3), 2.23 (1H, d, *J* = 2.5, HOCC*H*H), 2.76 (1H, ddd, *J* = 8.2, 5.2, 2.5, HOCCH*H*), 3.22 (1H, dd, *J* = 12.3, 8.2, C*H*HN), 3.53 (1H, dd, *J* = 12.3, 5.2, CH*H*N), 6.70, 6.75, 7.19 (5H, 3m, 5xArH); δ_C 27.9 (2C, 2xCH_3), 43.4, 44.2 (*C*H_2C≡C*C*H_2N), 71.9, 72.7, 83.2 (*C*≡CCH_2*C*OH), 113.5, 118.1, 129.3, 147.7 (6C, ArC); *m/z* 204 (M^++1, 1.4%), 203 (M^+, 9), 107 (11), 106 (100), 93 (14), 79 (10), 77 (28), 59 (17), 51 (17), 43 (18) (Found: M^+, 203.1305. $C_{13}H_{17}NO$ requires M, 203.1310).

1-(4-Phenylamine-2-butynyl)cyclohexanol (**6be**): ν (film) 3393, 3297 (NH, OH), 3051, 3021, 1603, 1504 (C=CH), 2110 cm^{-1} (C≡C); δ_H 1.54-1.80 (10H, m, 5xring CH_2), 2.23 (1H, d, *J* = 2.4, HOCC*H*H), 2.76 (1H, def ddd, *J* = 8.5, 4.9, 2.4, HOCCH*H*), 3.26 (1H, dd, *J* = 12.2, 8.5, C*H*HN), 3.54 (1H, dd, *J* = 12.2, 4.9, CH*H*N), 6.67, 6.74, 7.20 (5H, 3m, 5xArH); δ_C 21.8, 25.6, 35.1, 35.3 (6C, 5xring CH_2 and *C*H_2COH), 43.2 (CH_2N), 72.4, 73.0, 83.1 (*C*≡CCH_2*C*OH), 113.5, 118.0, 129.25, 147.8 (6C, ArC); *m/z* 244 (M^++1, 0.7%), 243 (M^+, 3.4), 106 (100), 105 (16), 104 (10), 93 (14), 77 (27), 55 (14), 51 (16), 44 (18), 43 (10), 42 (12) (Found: M^+, 243.1634. $C_{16}H_{21}NO$ requires M, 243.1623).

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11. For this product was not possible to obtain the corresponding HRMS due to its decomposition and/or to the low intensity of the M^+.

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